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# Vibrating boron-doped diamond electrode: A new, durable and highly sensitive tool for the detection of cadmium

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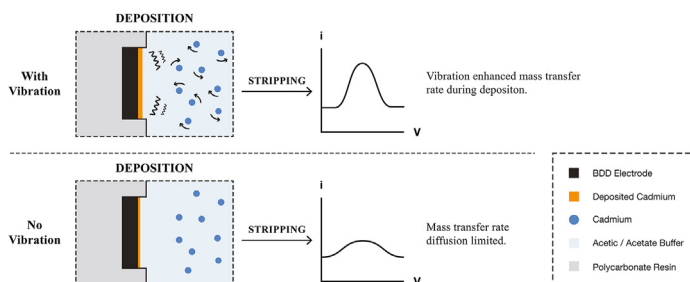
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## HIGHLIGHTS

- Novel vibrating analytical method for ultralow concentrations of Cd(II).
- Accurate and reproducible analytical method without electrode modification.
- LOD and LOQ for Cd(II) analysis were 0.04  $\mu\text{g L}^{-1}$  and 0.12  $\mu\text{g L}^{-1}$ , respectively.
- Applicability of the method was successfully verified by analysis of river samples.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper, a vibrating boron-doped diamond (BDD) electrode electroanalytical device and respective method for the analysis of ultralow concentrations of Cd(II) in water were studied. The enhanced mass transfer on the electrode surface was studied using  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ . Vibration with 133 Hz frequency enhanced the Ru(III) to Ru(II) reduction by 92.6% compared to a static electrode. The peak current of the anodic stripping voltammetry (ASV) method employed was increased by a factor of 5.3 and 4.7 for 10 and 30  $\mu\text{g L}^{-1}$  Cd(II) concentrations, respectively, when a frequency of 200 Hz was used. A calibration plot with two linear regions was resolved between 0.01 and 1  $\mu\text{g L}^{-1}$  and 1–30  $\mu\text{g L}^{-1}$  with the LOD and LOQ of 0.04  $\mu\text{g L}^{-1}$  and 0.12  $\mu\text{g L}^{-1}$ , respectively. The applicability of the device and the respective method in the analysis of real environmental samples was successfully verified by analysis of river samples and comparing the results with the ICP analysis presenting high reproducibility and trueness. According to the results of this research, the vibrating BDD electrode with the ASV method has excellent analytical performance without surface modification or regular replacement or polishing of the electrode surface. Combining the exceptional electrochemical and chemical properties of BDD with enhanced mass transfer and signal strength of vibrating electrodes makes the system especially suitable for on-site and online analysis of heavy metals.

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## 1. Introduction

Excess exposure to heavy metal ions, including Pb(II), Cd(II) and Hg(II), has health effects on people and fauna [1,2]. In many areas of the world, these metals exist naturally in water through natural processes. However, heavy metal pollution is also caused by industrial activities, such as mining and chemical production. Heavy metals can induce various health concerns including cancer, neurological, cardiovascular, and development issues [1,3,4]. Usually, exposure to heavy metals is controlled in high-income countries through water treatment processes and monitoring of water quality but in developing countries, exposure to heavy metals is a common cause of health issues. In this regard, WHO has set guideline values for the heavy metal concentrations in drinking water including Cd(II)  $3 \mu\text{g L}^{-1}$ , Pb(II)  $10 \mu\text{g L}^{-1}$ , and Hg(II)  $6 \mu\text{g L}^{-1}$  (inorganic mercury).

Heavy metals in water are typically analysed by collecting a sample and analysing it in a laboratory using AAS or ICP-MS. However, these techniques cannot be used for on-site or online monitoring. Frequent monitoring with other techniques is beneficial when heavy metal concentration varies due to industrial discharges or seasonal effects, such as rainfall. Electrochemical techniques are suitable for low-cost on-site and online analysis of various water pollutants, including heavy metals. The most commonly used electroanalytical techniques are voltammetric [5–7] and potentiometric methods [8,9].

Historically, mercury drop electrodes were most commonly used for heavy metal analysis but alternative materials, such as bismuth, antimony and diamond materials, have been researched due to the toxicity and environmental issues of mercury [5]. Among them, boron-doped diamond (BDD) has several favourable properties compared to other electrode materials, such as a wide solvent window, chemical stability in challenging environments, mechanically robust, and reduced fouling [10–13]. Due to its exceptional electrochemical properties, BDD has been widely used in the voltammetric analysis of various analytes since the use of mercury electrodes is not recommended. When used as electrode material in anodic stripping voltammetry (ASV) it has been shown to be a suitable alternative to mercury in the heavy metal analysis of Cd(II), Pb(II), Hg(II), Cu(II) [14–17]. It has been generally shown that BDD is comparable to mercury electrodes when doping level, non-diamond carbon proportion, surface termination, and crystal size are suitable for electroanalytical applications.

On the other hand, mass transfer of the deposition step of stripping voltammetry can be enhanced by vibrating the electrode surface [18–21]. Commonly vibration has been combined with gold microelectrodes. In this regard, Chapman and van der Berg used vibrating gold microelectrodes for ASV analysis of Cu(II) [20]. It has been demonstrated that by vibrating the microwire, the sensitivity was enhanced by 3–4 times compared to a standard rotatory stirrer. Alves et al. developed a method for simultaneous determination of As(V), Cu(II), Pb(II), and Hg(II) with DPASV on a vibrating gold microwire electrode [18]. The vibration of the electrode improved the sensitivity and reproducibility of the results. Detection limits (LODs) of the metals were in the range of  $\text{nmol L}^{-1}$ . However, it is well known that there is a gradual change of gold electrode surface when the electrode is used for continuous measurements and, hence, surface renewal is required by the application of extreme oxidation or reduction potentials, the use of cleaning solutions and/or the polishing of the surface [22]. To the best of our knowledge, no literature exists regarding the combination of vibration with BDD, which will be one of the important goals of the present work.

Thus, in this research, a vibrating BDD electrode was developed

taking advantage of both the BDD exceptional material properties for electroanalytical measurements and the enhancement of the mass transfer during the deposition step of ASV provided by the vibrating motor. The developed vibrating BDD electrode was microscopically and analytically described, and applied for the voltammetric determination of Cd(II) in river water samples.

## 2. Experimental section

### 2.1. Materials and reagents

The polycrystalline boron-doped diamond (BDD) electrode was purchased from Element 6, Ltd. ( $10 \times 10 \text{ mm}$ , Electrochemical Grade, Japan) and has a trace of non-diamond carbon (NDC) according to Raman spectra (RENISHAW inVia, England) as shown in Fig. 1, typical boron doping concentration of  $2\text{--}6 \times 10^{20}$  boron atoms  $\text{cm}^{-3}$  and resistivity of  $0.2\text{--}1.8 \times 10^{-3} \Omega \text{ m}$ . Cadmium Standard for ICP ( $1000 \text{ mg L}^{-1}$  in 2% nitric acid), glacial acetic acid, sulfuric acid, potassium nitrate and reagent grade sodium hydroxide were purchased from Merck (Germany). Sodium acetate trihydrate (min. assay 99.0%) was purchased from VWR International (USA). Milli-Q water (electrical resistivity  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ) was collected from a Synergy® UV Water Purification System (USA) and used to prepare all solutions in this work.

Cyclic voltammetry (CV) was conducted with the vibrating BDD electrode in a solution of  $2 \text{ mol L}^{-1}$  hexaammineruthenium(III) chloride ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ ) in  $1 \text{ mol L}^{-1}$  potassium nitrate.  $0.2 \text{ mol L}^{-1}$  acetate buffer with pH 4.5 was prepared and used as the background solution in square-wave anodic stripping voltammetry (SWASV) experiments in order to control the pH. Stock solutions were prepared from ICP cadmium standards and acetate buffer.

The river water was collected from Merri Creek (Victoria, Australia) for Cd(II) analysis using the standard addition method. ICP-MS analysis was conducted using a Varian 7700 (USA) to determine the Cd(II), Cu(II) and Pb(II) concentrations. The river water constituent concentrations were  $0.03 \mu\text{g L}^{-1}$  Cd(II),  $4 \mu\text{g L}^{-1}$  Cu(II) and  $0.6 \mu\text{g L}^{-1}$  for Pb(II). As the Cd(II) concentration determined was less than the LOD obtained for the vibrating BDD electrode, the river water sample was spiked with Cd(II) prior to standard addition measurements. ICP-MS on three spiked river water samples confirmed an average total Cd(II) concentration of  $0.14 \mu\text{g L}^{-1}$  and a standard deviation of  $0.1 \mu\text{g L}^{-1}$ .

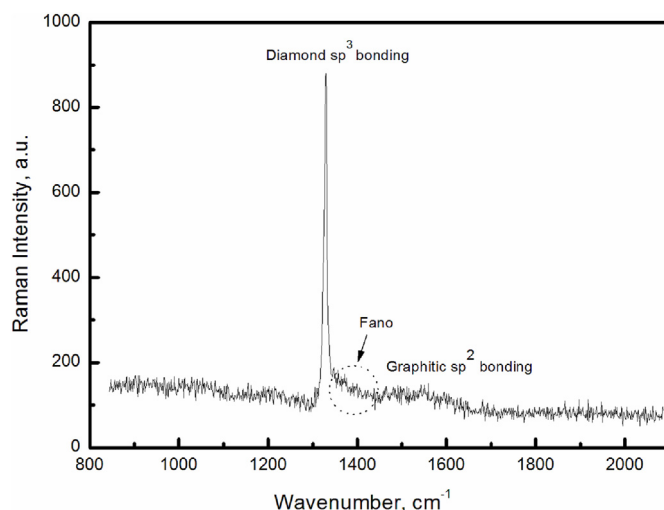


Fig. 1. Raman spectra of Element 6 BDD with diamond  $\text{sp}^3$  and graphitic  $\text{sp}^2$  areas identified. Fano interference appears in highly boron-doped diamond electrodes.

## 2.2. Vibrating BDD electrode design and preparation

The design of the vibrating BDD electrode comprises a component containing the BDD electrode and a separate component for the vibrating motor which allows for interchangeability should a component fail. These components, made from polycarbonate, were connected to form the sensing device. The components were designed in SolidWorks 2019 and manufactured using a CNC milling machine by Arptech, Pty. Ltd. The design of the vibrating sensing device and the experimental setup is illustrated in Fig. 2. The geometric area of the BDD surface exposed to the solution was  $0.48 \text{ cm}^2$ . The BDD surface was cleaned by rinsing with ethanol and Milli-Q water, then left to dry before being inserted and glued into the polycarbonate component with epoxy resin (EpoFix Resin, Struers, Inc.). Once dry, hook-up wire ( $0.33 \text{ mm}^2$  cross-sectional area, RS Components, Inc., UK) was attached to the back-side of the BDD electrode by conductive silver adhesive epoxy (RS 186–3616, RS Components, Inc., UK) and air-dried. Epoxy resin was again used to seal the mould. Similarly, the vibrating motor was placed inside the polycarbonate component and epoxy resin was used to seal the mould.

## 2.3. Voltammetric measurements

A PalmSens4 potentiostat was used for all electrochemical measurements running PSTrace software (version 5, PalmSens). A conventional three-electrode cell configuration was used and all measurements were conducted at room temperature without deaeration. The vibrating BDD electrode, a platinum coated titanium rod (5 mm diameter, 50 mm length, NMT Electrodes Pty Ltd, Australia) and Ag/AgCl (sat KCl, Koslow Scientific, USA) were used as the working, counter and reference electrodes, respectively. All electrochemical measurements were conducted in a standard 250 mL borosilicate glass beaker at room temperature. A cylindrical DC vibration motor (maximum frequency 200 Hz at 3 V,  $8.8 \times 25 \text{ mm}$ , Jinlong Machinery & Electronic Co., Ltd., China) and a bench power supply (EL302R bench power supply, Aim-TTi, UK) was used to control the vibrating BDD working electrode.

To ensure reproducibility of results at low Cd(II) concentration, the BDD electrode surface was cleaned between measurements. This was achieved by rinsing the BDD electrode with Milli-Q water, then conducting CV in 0.1 M sulfuric acid for 20 scans between 0.2 and 1.0 V at a scan rate of  $50 \text{ mV s}^{-1}$ .

CV was used to determine the effect of the vibration and the scan rate on the current response of the vibrating BDD electrode. CV was conducted in  $0.2 \text{ mM Ru}(\text{NH}_3)_6\text{Cl}_3$  in  $1 \text{ mol L}^{-1} \text{ KNO}_3$  solution between  $-1.0 \text{ V}$  and  $0.6 \text{ V}$  with a start potential of  $0 \text{ V}$  vs. OCP. A scan rate of  $25 \text{ mV s}^{-1}$  was used when motor vibration frequencies were varied, and  $100 \text{ Hz}$  vibration frequency was used when the scan rate was varied.

The SWASV parameters were optimised in acetate buffer solutions for Cd(II) concentrations of  $1 \mu\text{g L}^{-1}$  and  $10 \mu\text{g L}^{-1}$ . The selected parameters were: conditioning potential ( $E_{\text{cond}}$ ) of  $0.5 \text{ V}$  applied during a conditioning time ( $t_{\text{cond}}$ ) of  $45 \text{ s}$ , deposition potential ( $E_d$ ) of  $-1.3 \text{ V}$ , deposition time ( $t_d$ ) of  $300 \text{ s}$ , equilibration time of  $10 \text{ s}$ , potential range of  $-1.3 \text{ V}$ – $0 \text{ V}$ , with frequency ( $\nu$ ) of  $30 \text{ Hz}$ , modulation amplitude ( $E_{\text{SW}}$ ) of  $50 \text{ mV}$  and step potential of  $8 \text{ mV}$ .

The linear calibration plots for Cd(II) determination by SWASV on vibrating BDD electrode were performed by increasing the Cd(II) concentration in a  $0.2 \text{ mol L}^{-1}$  acetate buffer solution (pH 4.5).

For Cd(II) determination in real water samples,  $0.2 \text{ mol L}^{-1}$  acetate buffer solution was added to a volume of Cd(II) spiked river water sample to ensure a pH value of 4.5 (dilution factor 1/2) before SWASV measurements. The standard addition method was used for calibration by successively adding four aliquots containing Cd(II) standard solution.

## 3. Results and discussion

### 3.1. Cyclic voltammetry with standard redox couples

Mass transfer rate at the vibrating electrodes is known to be enhanced compared to static electrodes. Gomaa et al. have shown that the amplitude and frequency of the vibration affect the mass transfer and up to 23-fold enhancement of the mass transfer can be obtained [23]. In this paper, the mass transfer enhancement was studied by CV in hexaammineruthenium(III) chloride solutions in varied vibration frequencies and scan rates.

$\text{Ru}^{3+}$  reduction on the BDD electrode was initially measured on a stationary electrode with varying scan rates (Fig. 3a). Peak-peak separation was  $90 \text{ mV}$  at the scan rate of  $25 \text{ mV s}^{-1}$  and no significant peak shift was observed indicating close to ideal electron transfer kinetics. Increasing vibration frequency transforms the cyclic voltammogram from a typical shape with two distinguishable peaks to one with enhanced mass transfer and limiting current similar to obtained on a rotating disc electrode. The current density at  $-1 \text{ V}$  vs. Ag/AgCl (sat) increases from  $95 \mu\text{A cm}^{-2}$  to  $183 \mu\text{A cm}^{-2}$  when the frequency is increased from  $0 \text{ Hz}$  to  $133 \text{ Hz}$  (Fig. 3b). This is due to the enhanced mass transfer of the  $\text{Ru}^{2+}/\text{Ru}^{3+}$  redox species on the electrode surface. Enhanced mass transfer is beneficial for metal deposition during the cathodic deposition stage of SWASV.  $200 \text{ Hz}$  frequency is not shown in the figure due to noisy data. However,  $200 \text{ Hz}$  was applicable in the analytical method because the noise was averaged over the whole deposition time and did not affect the performance of the system as is shown in the statistical analysis of this paper.

### 3.2. Analytical performance evaluation

The effects of deposition settings and SWASV parameters on the voltammetric response on the vibrating BDD electrode were assessed by conducting SWASV in solutions containing  $1$  and  $10 \mu\text{g L}^{-1}$ . The deposition potential ( $E_d$ ) was studied between  $-0.9$  and  $-1.3 \text{ V}$ , and the deposition time ( $t_d$ ) between  $120$  and  $300 \text{ s}$ . As for the square wave scans, the frequency ( $\nu$ ) was studied between  $10$  and  $75 \text{ Hz}$  and the potential amplitude ( $E_{\text{SW}}$ ) between  $10$  and  $80 \text{ mV}$ . First  $E_d$  was optimised, with  $-1.3 \text{ V}$  leading to the maximum

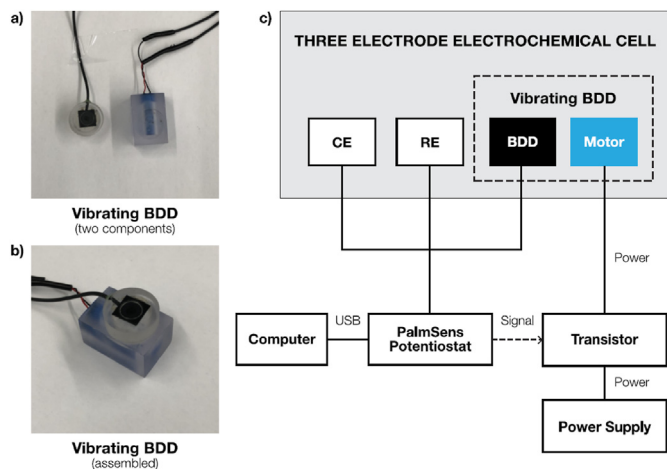
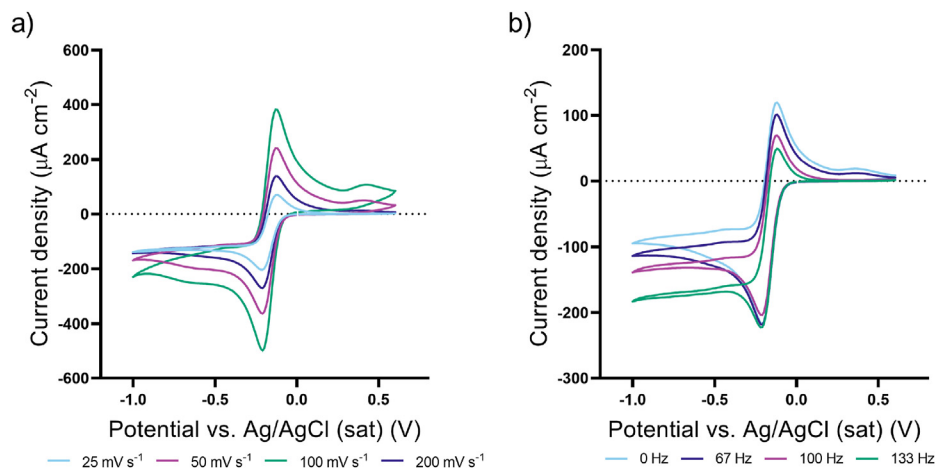


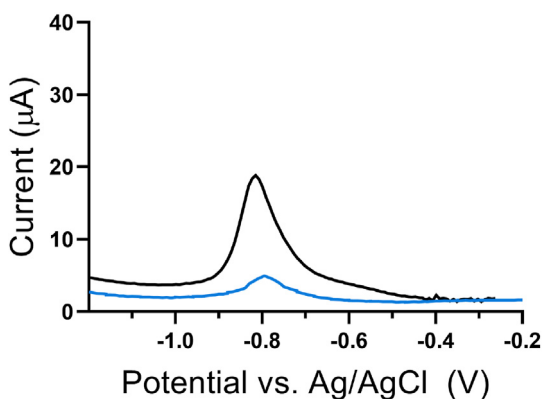
Fig. 2. Photos depicting the vibrating BDD electrode and components: a) BDD electrode and motor as two components; b) vibrating BDD electrode assembled; c) schematic depicting experimental setup.



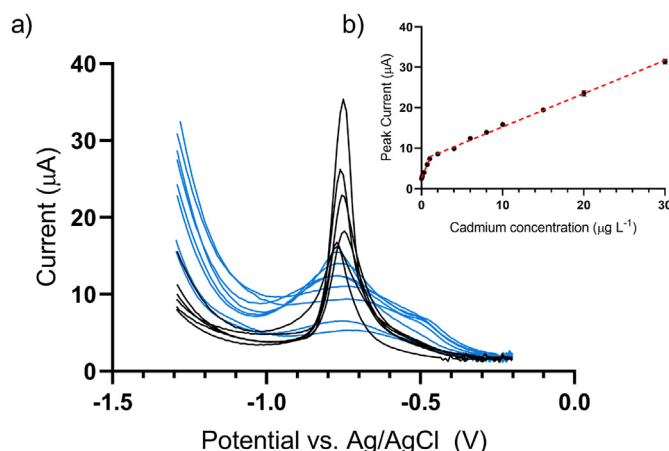
**Fig. 3.** CV with vibrating BDD electrode in  $0.2 \text{ mmol L}^{-1} \text{ Ru}(\text{NH}_3)_3\text{Cl}_3$  in  $1 \text{ mol L}^{-1} \text{ KNO}_3$  solution: a) scan rate varied between  $25 - 200 \text{ mV s}^{-1}$  with vibration frequency  $100 \text{ Hz}$ ; b) vibration frequency varied between  $0 - 133 \text{ Hz}$  with  $25 \text{ mV s}^{-1}$  scan rate.

peak height which was selected for further optimisation experiments. A  $t_d$  of  $300 \text{ s}$  was selected as this led to the greatest peak height while remaining within an acceptable analysis time. Finally,  $\nu$  of  $30 \text{ Hz}$  and  $E_{\text{SW}}$  of  $50 \text{ mV}$  were selected as suitable SWASV parameters. A  $200 \text{ Hz}$  motor vibration frequency was used to significantly enhance the mass diffusion of  $\text{Cd}(\text{II})$  metal ions to the BDD surface. The effect of vibration on the current response is illustrated in Fig. 4, where the SWASV response for no vibration (blue line) and at  $200 \text{ Hz}$  (black line) is displayed at  $10 \mu\text{g L}^{-1}$ . It was observed that the peak current was increased by a factor of  $5.3$ . The increase in the peak current of the vibrating electrode clearly creates effective stirring at the BDD electrode surface as a result of the high-frequency vibrations that significantly enhance mass transport.

Calibration of the vibrating BDD electrode for  $\text{Cd}(\text{II})$  metal ion detection was performed in triplicate with the sensing device electrochemically cleaned in sulfuric acid solution between measurements to ensure measurement accuracy, especially at ultra-low  $\text{Cd}(\text{II})$  concentrations. Calibration plots were obtained for  $\text{Cd}(\text{II})$  concentrations ranging from  $0.01$  to  $30 \mu\text{g L}^{-1}$  using the optimised settings in  $0.2 \text{ mol L}^{-1}$  acetate buffer solution at  $\text{pH } 4.5$ . Representative SWASV measurements and the corresponding calibration plot is shown in Fig. 5a and Fig. 5b, respectively. From the calibration plot, two linear regions with two types of peak responses can



**Fig. 4.** SWASV measurement with  $200 \text{ Hz}$  vibration frequency (black line) and without vibration (blue line) at  $10 \mu\text{g L}^{-1} \text{ Cd}(\text{II})$  concentration in  $0.2 \text{ mol L}^{-1}$  acetate buffer  $\text{pH } 4.5$  using  $E_d = -1.3 \text{ V vs. Ag/AgCl}$  and  $t_d = 300 \text{ s}$ .



**Fig. 5.** a) SWASV measurements for calibration of  $\text{Cd}(\text{II})$  in  $0.2 \text{ mol L}^{-1}$  acetate buffer at  $\text{pH } 4.5$  using a vibrating BDD electrode at  $E_d = -1.3 \text{ V vs. Ag/AgCl}$  and  $t_d = 300 \text{ s}$  with  $200 \text{ Hz}$  vibration frequency. Two types of peak responses can be observed: flat and broad (blue), and sharp and narrow (black). b) calibration curves obtained for  $\text{Cd}(\text{II})$  concentration between  $0.01$  and  $30 \mu\text{g L}^{-1}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

be resolved between  $0.01$  and  $1 \mu\text{g L}^{-1}$  (flat and broad peaks) and  $1-30 \mu\text{g L}^{-1}$  (sharp and narrow peaks). We hypothesise that this different type of peak response could be attributed to the fact that at low  $\text{Cd}(\text{II})$  concentrations (blue peaks) the interactions between the reduced metal and the BDD surface are stronger than those that take place at higher  $\text{Cd}(\text{II})$  concentrations (black peaks) when the BDD surface is coated with a considerable amount of metallic atoms.

**Table 1**

Analytical performance of  $\text{Cd}(\text{II})$  detection by SWASV using a vibrating BDD electrode at  $E_d = -1.3 \text{ V vs. Ag/AgCl}$ ,  $t_d = 300 \text{ s}$  in  $0.2 \text{ mol L}^{-1}$  acetate buffer at  $\text{pH } 4.5$ . Standard deviation displayed within the brackets.

	First linear region	Second linear region
Sensitivity ( $\mu\text{A } \mu\text{g}^{-1} \text{ L}$ )	4.8 (0.1)	0.82 (0.01)
Intercept ( $\mu\text{A}$ )	2.62 (0.06)	7.1 (0.2)
$R^2$	0.998	0.998
Linear Range ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	0.12–1	1–30
LOD ( $\mu\text{g L}^{-1}$ )	0.04	–

<sup>a</sup> The lowest level of the linear range was established from the LOQ.



**Table 2**

Repeatability and reproducibility results (expressed as percent relative standard deviation) for Cd(II) determination by SWASV with a vibrating BDD electrode at  $E_d = -1.3$  V vs. Ag/AgCl,  $t_d = 300$  s and pH 4.5.

<b>Reproducibility</b> (N = 15)	
At $1 \mu\text{g L}^{-1}$	6.3
At $10 \mu\text{g L}^{-1}$	4.8
<b>Repeatability</b>	
120 s $t_d$ in first linear region	5.0
120 s $t_d$ in second linear region	6.9
300 s $t_d$ in first linear region	1.2
300 s $t_d$ in second linear region	2.9

**Table 3**

Summary of various boron-doped diamond-based electrodes for the determination of Cd(II).

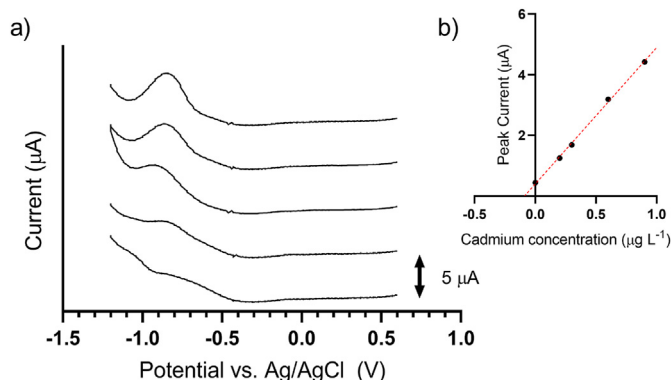
Electrode	Technique	Linear range ( $\mu\text{g L}^{-1}$ )	LOD ( $\mu\text{g L}^{-1}$ )	Deposition time (s)	Ref.
Boron-doped diamond electrode	SWASV	28.1 – 337.2	0.44	60	[28]
Boron-doped diamond electrode	SWASV	10 – 50	10	300	[29]
Boron-doped diamond films deposited on conductive silicon substrates	DPASV	112.4 – 562.0	28.1	120	[30]
Boron-doped diamond thin-film electrode	DPASV	10 – 1000 <sup>a</sup>	1.0	210	[15]
Nanocrystalline boron-doped diamond electrode	DPASV	1.2 – 25 <sup>b</sup>	0.36 <sup>b</sup>	60	[31]
		3.2 – 70 <sup>c</sup>	1.0 <sup>c</sup>		
Bismuth nanoparticle modified boron-doped diamond electrode	SWASV	0.05 – 20	2.3	120	[32]
Antimony nanoparticle modified boron-doped diamond electrode	LSASV	50 – 500	38.1	120	[17]
Boron-doped diamond electrode	DPASV	10 – 100	3.5	300	[33]
Boron-doped diamond electrode	LSASV	0 – 1124.1	10	60	[34]
Boron-doped diamond microcell	DPASV	0 – 3.9	0.04	20	[35]
Polyphenol-polyvinyl chloride – boron-doped diamond electrode	DPASV	0.0025 – 11.8	0.0025	20	[36]
Vibrating boron-doped diamond electrode	SWASV	0.12 – 1.0; 1 – 30	0.04	300	This work

DPASV: differential pulse anodic stripping voltammetry; LSASV: linear sweep anodic stripping voltammetry; SWASV: square wave anodic stripping voltammetry.

<sup>a</sup> Denotes largest concentration measured and is not necessarily the upper limit.

<sup>b</sup> 0.01 mol L<sup>-1</sup> acetate buffer.

<sup>c</sup> 0.1 mol L<sup>-1</sup> acetate buffer.



**Fig. 6.** a) SWASV measurements in a river water sample in  $0.2 \text{ mol L}^{-1}$  and pH 4.5 (dilution factor 0.5) using a vibrating BDD electrode with  $E_d = -1.3$  V and  $t_d = 300$  s. b) Corresponding calibration plot according to the standard addition method.

**Table 4**

SWASV determination of Cd(II) in river water on a vibrating BDD electrode by the standard addition method with an  $E_d = -1.3$  V and  $t_d = 300$  s at pH 4.5.

	Cd(II) concentration ( $\mu\text{g L}^{-1}$ )	RSD (%) N = 3	Relative error (%)
Vibrating BDD	0.16	2.8	14.4
ICP verified value	0.14	7.2	–

The calibration data for the vibrating BDD electrode is summarised in Table 1. The LOD and LOQ are defined to be three and ten times the standard deviation of the intercept over the slope and were calculated to be  $0.04 \mu\text{g L}^{-1}$  and  $0.12 \mu\text{g L}^{-1}$ , respectively.

Table 2 summarizes the repeatability and reproducibility of the

proposed methodology, which always yields dispersions below 7.0%. These figures are especially good inside the first linear region (the most sensitive) and using a deposition time of 300 s (repeatability 1.2% and reproducibility 6.3%).

These results signify the excellent capabilities of the vibrating BDD device for Cd(II) detection owing to the electrochemical properties of BDD as well as the enhanced mass diffusion to the electrode surface induced by the vibration. These features are especially remarkable when compared to those of non-vibrating BDD electrodes found in the literature (Table 3). Thus, compared to those reported using BDD based electrodes, the LOD and LOQ obtained using the vibrating BDD electrode are considerably lower than most of those provided in the literature with the additional advantage that the BDD surface is not modified. Moreover, the LOD and LOQ achieved by the vibrating BDD electrode are also much lower than those obtained by most of the bismuth-based electrodes and antimony based electrodes, two renowned electrodes for Cd(II) determination [24,25].

Therefore, taking into account the excellent analytical performance displayed by the vibrating BDD electrode coupled with the fact that the achieved LOD is well below the Cd(II) guideline values of the World Health Organisation (WHO) and Australian Drinking Water Guidelines (ADWG) of  $3 \mu\text{g L}^{-1}$  and  $2 \mu\text{g L}^{-1}$ , respectively, it can be concluded that the developed vibrating BDD electrode would be fully suitable for the monitoring of metal ions at ultra-low concentration levels in natural samples [26,27].

### 3.3. Real sample measurements

The vibrating BDD electrode for the detection of Cd(II) in the presence of other metal ions such as Pb(II) and Cu(II) was assessed in a river water sample. The standard addition method was applied for Cd(II) determination. Fig. 6a displays typical SWASV responses with increasing Cd(II) concentration from bottom to top.

A representative standard addition plot is displayed in Fig. 6b, showing good linearity over the concentration range. Table 4 summarizes the concentration data for Cd(II) determination obtained from three replicates of the standard addition method. Considering the low Cd(II) concentration, a relatively good agreement was obtained between the ICP verified Cd(II) concentration and that obtained with the vibrating BDD electrode. Additionally, determination of the relative error using the lower limit (one standard deviation below) of the vibrating BDD Cd(II) concentration and the upper limit (one standard deviation above) of the ICP verified Cd(II) concentration yields 3.9%. It should be mentioned that this river water sample also contains other metal ions such as lead ( $0.6 \mu\text{g L}^{-1}$ ) and copper ( $4 \mu\text{g L}^{-1}$ ), which do not seem to interfere in the SWASV determination of Cd(II) using the vibrating BDD electrode. Thus, these results indicate that the vibrating BDD electrode is suitable for voltammetric measurement of very low Cd(II) concentrations in natural samples.

#### 4. Conclusions

In this paper, a vibrating BDD device and an electroanalytical method were developed for the analysis of ultralow concentrations of Cd(II). The main conclusions based on the results are the following:

- The vibration enhanced the mass transfer on the BDD electrode surface. The current density of the reduction reaction of  $\text{Ru}^{3+}$  (hexammineruthenium(III) chloride) at  $-1 \text{ V}$  increased from  $95 \mu\text{A cm}^{-2}$  to  $183 \mu\text{A cm}^{-2}$  with  $0 \text{ Hz}$  and  $133 \text{ Hz}$ , respectively, equal to 92.6% increase.
- The metal deposition was enhanced during the cathodic step of the ASV. The peak current was increased by a factor of 5.3 and 4.7 for  $10$  and  $30 \mu\text{g L}^{-1}$  Cd(II) concentrations, respectively, when a frequency of  $200 \text{ Hz}$  was used instead of static mode.
- A calibration plot with two linear regions was resolved between  $0.01\text{--}1 \mu\text{g L}^{-1}$  and  $1\text{--}30 \mu\text{g L}^{-1}$ . The LOD and LOQ were calculated to be  $0.04 \mu\text{g L}^{-1}$  and  $0.12 \mu\text{g L}^{-1}$ , respectively. The repeatability was 1.2% and reproducibility 6.3%.
- The device and the analytical method with standard additions were tested for the Cd(II) analysis of river water and compared with ICP analysis results. The Cd(II) concentrations were  $0.16 \mu\text{g L}^{-1}$  and  $0.14 \mu\text{g L}^{-1}$  according to ASV and ICP method, respectively, demonstrating the applicability of the device and method for the analysis of real environmental samples.

The vibrating BDD device studied in this paper has several benefits over the other analytical devices and methods applied or proposed for heavy metals. The small size of the device has benefits in on-site or online analysis while chemical stability of the BDD enables in-situ cleaning of the electrode with acid or electrochemical methods. The excellent analytical performance achieved with the device without surface modification or replacement of the electrode surface further points towards the applications in on-site or online monitoring of water quality.

#### CRedit authorship contribution statement

**Adam Morris:** Methodology, Investigation, Visualization, Formal analysis, Writing – original draft. **Núria Serrano:** Conceptualization, Methodology, Resources, Supervision, Formal analysis, Writing – review & editing. **José Manuel Díaz-Cruz:** Conceptualization, Methodology, Resources, Supervision, Formal analysis, Writing – review & editing. **Avi Bendavid:** Methodology, Investigation, Writing – review & editing. **Miao Chen:** Methodology, Resources. **Mikko Vepsäläinen:** Conceptualization, Methodology,

Resources, Supervision, Writing – review & editing, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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